Core-Mantle Equilibrium: Comments on a Paper by R. Brett

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Abstract

Brett's arguments are critically reviewed. It is con-
cluded that the abundances of Ni, Co, Cu, Au and Pt in the upper
mantle, the oxidation state of this region and the nature of the
volatiles inferred to have been degassed from the upper mantle
are not readily explained if the earth has accreted from a well
mixed reservoir of preexisting metal and silicate particles in the
solar nebula which were equilibrated within the earth prior to
separation of the core. The data can be readily explained if it
is assumed that the earth accreted inhomogeneously in a state
which was initially out of overall chemical equilibrium and that
equilibrium, although approached, was not finally achieved during
core-segregation.

1) Introduction

Most of Brett's paper is devoted to criticism of conclusions concerning core-mantle equilibrium reached by me in an earlier paper published in this Journal (Ringwood, 1966a, see also Ringwood 1966b). As was emphasized in these papers, the topic has a crucial bearing upon that most fundamental of all earth science problems - the origin of the earth, and clearly warrants an intensive and critical study.

Many well-known theories of the origin of the earth maintain that a high temperature episode occurred in the parental solar nebula before accretion of the earth, leading to the formation of metallic nickel-iron particles and silicate particles and that the earth accreted from this preexisting mixture of metal particles and silicate particles. After accretion, partial or complete melting of the earth occurred and the metal segregated to form the core. The conclusion reached in my 1966 papers and criticized by Brett was that the present chemical composition of the mantle is inconsistent with this hypothesis which implies that local chemical equilibrium was reached between metal and silicates prior to core-segregation.

2) Partition of some metals between core and mantle

It was shown by Ringwood (1966b)[1] and independently by Duke (1965) that the abundance of nickel in the upper mantle is 10 to 100

[1]Submitted for publication September, 1964.

times higher than would be expected from equilibrium considera-
tion if this region had once equilibrated with metallic iron which
had subsequently segregated into the core. The equilibrium partition
coefficients were inferred from electronmicroprobe data on coexisting
ferromagnesian minerals and metal in meteorites, and from experimental
data. Ringwood (1966a,b) concluded that the same pattern was followed
by Co, Cu, Au and Pt. The equilibrium partitions for Co and Cu
were inferred from meteoritic data. For Au and Pt, my conclusion
followed from the assumption that the metal/silicate partitions
would not be <u>smaller</u> than the corresponding values for nickel. This
assumption was based upon the general chemical and thermodynamic
properties of these elements and their compounds, particularly the
relative instability of their oxycompounds, as a result of which
gold and platinum are regarded as being more "noble" than nickel.
Although this assumption has yet to be tested by experiment, I still
believe that it is very likely to be correct.

Brett, pp. 18, 22, concedes that Ni, Co and Cu are considerably
enriched in the upper mantle compared to abundances to be expected
on the basis of metal-silicate partition equilibria. On the other
hand he concludes that abundances of Au, Pt, Ir and Re in the upper
mantle are consistent with an equilibrium partition model. His con-
clusion is based upon partition coefficients derived from bulk
chemical analyses of <u>physically separated</u> metal and silicate fractions

from chondrites and occasionally, pallasites. Those who are familiar with chondrites are well aware that it is impossible to obtain a complete separation of metal from silicate by physical methods owing to the wide distribution of minute metallic particles as inclusions in silicates. The problem in the case of pallasites is less severe, but nevertheless is still present. The abundances of Au, Pt, Ir and Re measured in the silicate fraction are on the order of a few parts per billion. Abundances of this order are readily explained by the presence of less than one percent of contaminating metal phase. Silicate-metal partition coefficients obtained by this method provide only upper limits to the correct values, and Brett's application of these data in the present case is entirely without justification.

My conclusion that the abundances of Ni, Co and Cu are excessive in the upper mantle compared to abundances based upon an equilibrium metal-silicate partition model is unchallenged. Provided that the corresponding metal/silicate partition coefficients for Au and Pt not less than those of nickel, the same conclusion applies to these elements.

Clearly an explanation must be found for these discrepancies. Brett appeals to the effect of high pressures in the earth's interior upon the relevant partition coefficients which were determined at low pressure. This explanation was previously considered and rejected by me (Ringwood 1966a, p. 70). Several

authors have previously shown that the $P.\Delta v$ term may dominate

the free energy change of a metal-silicate partition equilibrium

in the deep mantle. However the sizes and signs of the relevant

partial molar volume changes are completely unknown for the

probable mineral assemblages which exist in the deep mantle

(Ringwood, 1970). It might be expected that the sizes of the

volume changes will vary by large amounts for different partition

equilibria and that the signs will fluctuate in an unsystematic

manner. The calculations presented by Brett on the effect of

pressure upon Ni-Fe partition equilibria are irrelevant to the

problem under consideration since neither the sign nor size of the

appropriate Δv change in the deep mantle is known, and the

mineral phases considered by Brett probably do not occur in the

deep mantle (Ringwood, 1970). The same objection applies to his

calculations on $Si-SiO_2$ equilibria.

If the overabundance of only one or two elements in the upper

mantle were under consideration, an explanation in terms of a

pressure effect would be worth considering. The significant thing

is that all of the siderophile elements for which data now exists

(i.e. Ni, Co, Cu, Au, Pt) appear to be overabundant in the upper

mantle compared to expectations based upon equilibrium metal-

silicate partitions. It would be highly coincidental (chance of

1 in 32) for pressure to affect all of these equilibria in the same

sense (i.e. Δv terms having the same sign). Furthermore, the

inference that the proportions (compared to primordial abundances) of Fe, Ni, Co, Cu and Au which have remained behind in the upper mantle are similar within an order of magnitude is difficult to explain in terms of an equilibrium theory (Ringwood, 1966a, p. 70).

Brett proposes an alternative explanation for the high abundance of copper in the upper mantle. He proposes that Cu has become enriched in the upper mantle by similar processes which may have been responsible for upward concentration of the "incompatible elements" Hf, Zr, Ti, Ta, Ba, La, Sr. However the reason for strong fractionation of the latter elements is that they have ionic radii and charges which inhibit their entry into the principal mantle minerals. Copper does not belong in this group since its radius and charge (Cu^{2+}) are similar to Fe^{2+} and copper is readily able to enter ferromagnesian minerals replacing iron (and calcium). Strong vertical fractionation of copper in the mantle is also incompatible with Brett's method of explaining the high nickel content of the upper mantle since his mechanism specifically requires that the mantle has been well stirred and homogenized by convection.

Further data on the abundances of other relatively non-volatile siderophile elements combined with experimental determinations of partition coefficients are urgently required. It will be interesting to see whether they follow the pattern displayed by Ni, Co, Cu, Au and Pt.

3) Oxidation state of the mantle

Ringwood (1966a) pointed out that the oxidation states, as indicated by Fe^{3+}/Fe^{2+} ratios of unaltered basaltic rocks and of presumed upper mantle rocks were much higher than would be expected if upper mantle rocks had equilibrated with metallic iron at high temperatures and the iron had subsequently sunk into the core. Brett attacks this conclusion on two grounds. Firstly, he claims that observed Fe^{3+}/Fe^{2+} ratios in terrestrial basalts and peridotites do not reflect the true state of oxidation of the upper mantle because of subsequent oxidation in the earth's crust. Secondly, he selects a single wet chemical analysis of a peridotite with low Fe^{3+} and claims that the oxidation state of this particular peridotite is consistent with equilibration with metallic iron at elevated temperatures.

It is of course well known that many basalts, dolerites and gabbros and most ultramafics become partially oxidized and hydrated in the crustal environment. However there are ways to avoid these effects and to obtain information on the original oxidation states. For example, it does not appear likely that the rapidly quenched fresh glass rims of young oceanic tholeiite pillows on the deep oceanic floors, (sometimes containing excess argon) can have been incorporated oxygen from their environment by a process which necessarily involves diffusion. The Fe^{3+}/Fe^{2+} ratios of such glasses are usually close to 0.1, which is more than

5 times higher than expectations on the basis of equilibration with metallic iron (Ringwood 1966a). It is most difficult to understand how the primary mineral assemblages of enormous mafic intrusions such as the Bushveldt, have become oxidized by their crustal environment. Where did the oxygen come from and how was it introduced? Brett offers no evidence in support of the process which he is advocating.

The primary oxidation states of ultramafic rocks occurring as intrusions and as xenoliths in kimberlites and alkali basalts cannot be safely inferred from total rock analyses owing to frequent secondary alteration. It is, however, a simple matter to separate pure, unaltered, primary mineral phases from such rocks and to analyze these. It would be difficult to maintain that all such pure, coarse, mantle minerals have been oxidized after their arrival in the crustal environment. Large numbers of analyses of primary orthopyroxenes, clinopyroxenes, garnets and spinels which have been separated from ultramafic rocks and eclogites of presumed mantle origin have been carried out. Ferric oxide is a significant component of all of these minerals. Fe^{3+}/Fe^{2+} ratios in primary orthopyroxenes and clinopyroxenes usually fall in the range 0.1 to 1.0 (e.g. Green, 1969; Dawson, 1969; Aoki and Kushiro, 1968) whilst the Fe^{3+}/Fe^{2+} ratios of primary spinels separated from ultramafic rocks average about 0.5 (e.g. Ross, Fosters and Myers, 1964; Green, 1964).

These terrestrial Fe^{3+}/Fe^{2+} ratios should be compared with

the Fe^{3+}/Fe^{2+} ratios of corresponding minerals from rocks which

have equilibrated with metallic iron at high temperatures - e.g.

the Apollo 11 basalt. Despite careful analytical work it has

not been possible to establish the presence of significant amounts

of Fe_2O_3 in pyroxenes and spinels from lunar basalts (e.g. Agrell

et at. 1970, Hafner and Virgo, 1970). An upper limit to the

Fe^{3+}/Fe^{2+} ratio in spinels is probably about 0.02 and in pyroxenes,

about 0.01. In spinels separated from chondritic meteorites the

upper limit is about 0.03 (Bunch et al., 1967). The contrast

between minerals from the two environments is striking and well

documented. I do not believe that there can be any reasonable

doubt that primary upper mantle rocks and primary basalts derived

from this region possess much higher Fe^{3+}/Fe^{2+} ratios than would

be expected if these rocks had equilibrated with metallic iron at

high temperatures.

In opposition to this conclusion, Brett cites a single

chemical analysis of the Tinaquillo peridotite. Quite apart from

the obvious possibility of errors in a single wet analysis where a

small amount of Fe_2O_3 was determined by difference, he ignores the

fact that the peridotite was dominantly composed of olivine which

excludes ferric iron from its lattice. The legitimate comparison

would have been of the pyroxenes and spinels separated from the

peridotite, with corresponding pyroxenes and spinels which have

equilibrated with iron (above). I invite Brett to produce a comparison on this basis.

Also in support of his position, Brett cites unpublished results by Sato on the oxygen fugacity of a single dredged Hawaiian tholeiite as determined by a novel technique. It is not possible for me to comment adequately on such evidence until it has been published. However, Brett states that the fugacity - temperature curve was close to that of the iron - wüstite buffer. This is substantially higher than the oxygen fugacity of the metallic iron — olivine $(Mg_{.9}Fe_1)_2SiO_4$ assemblage at corresponding temperatures owing to reduction of the activity of FeO by compound formation and solid solution in the olivine.

It would be possible to explain in principle the high Fe^{3+}/Fe^{2+} ratio of the upper mantle after segregation of the core if crystallization differentiation in the mantle had caused a strong enrichment (greater than ten-fold) of Fe^{3+} in the upper mantle relatively to Fe^{2+}. This explanation was considered and rejected by Ringwood (1966a, p. 69) on grounds which still appear valid to me and do not warrant repetition. In any case, the explanation is not available to Brett who requires that the mantle has been well mixed and homogenized by convection so as to transfer nickel from lower to upper mantle.

4) Degassing of volatiles from the mantle

It is widely considered that the principal volatile components liberated by degassing of the earth's mantle are H_2O and CO_2 (Rubey 1951, 1955; Holland, 1963). I pointed out that if the upper mantle had equilibrated with metallic iron which subsequently settled into the core, the oxygen fugacity would be about 10^{-13} atm at 1200° C and the principal gaseous species generated by degassing of the upper mantle at high temperatures should be CO and H_2 rather than CO_2 and H_2O. This conclusion follows from the work of Mueller (1964).

Brett apparently does not question this basic conclusion but argues that the composition of the volatiles derived from the mantle has been totally obscured by mixing with air, water and CO_2 from the crust, hydrosphere and atmosphere. But where did the earth's hydrosphere and atmosphere come from in the first place? If Brett accepts the standard hypothesis that the earth's excess volatiles, including the oceans and CO_2 (now occurring as sedimentary carbonate) have been ultimately derived by degassing of the mantle, then he is indulging in a circular argument. (If, on the other hand, he wishes to discard Rubey's hypothesis, he would encounter other difficulties which are discussed later).

Brett correctly points out that a mixture of H_2 and CO evolved from a high temperature magmatic source would on cooling yield $H_2O \pm CO_2$ by the reactions:

$$2 \; CO \; \rightarrow \; CO_2 + C$$

$$H_2 + CO \; \rightarrow \; H_2O + C \; ,$$
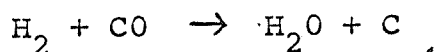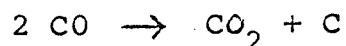
Formation of the earth's excess volatiles from primary H_2 and CO by these reactions requires that the mass of free carbon deposited in the upper crust should be similar to the mass of the entire hydrosphere. This is clearly contrary to observation.

5) Nature of the primitive atmosphere

One way to avoid some of these difficulties might be to assume that the earth's excess volatiles (mainly H_2O and CO_2) were present in the form of a massive primitive atmosphere immediately after the earth had formed. This would require abandonment of Rubey's hypothesis that the present atmosphere and hydrosphere has developed by gradual degassing of the mantle.

It does not appear to me to be possible to reconcile the presence of a large primitive atmosphere of H_2O and CO_2 with the widely accepted current hypothesis that the earth accreted from a preexisting mixture of iron particles and silicate particles in the solar nebula. According to advocates of this hypothesis (e.g. Brown, 1952; Larimer and Anders, 1967) the volatile components were either adsorbed on, or trapped in the silicate grains of the accreting material, or were present as a separate well-mixed "primitive" component, similar to Type 1 carbonaceous chondrites.

During most of the acretion of the earth, planetesimals are strongly heated and vapourized during impact due to liberation of gravitational 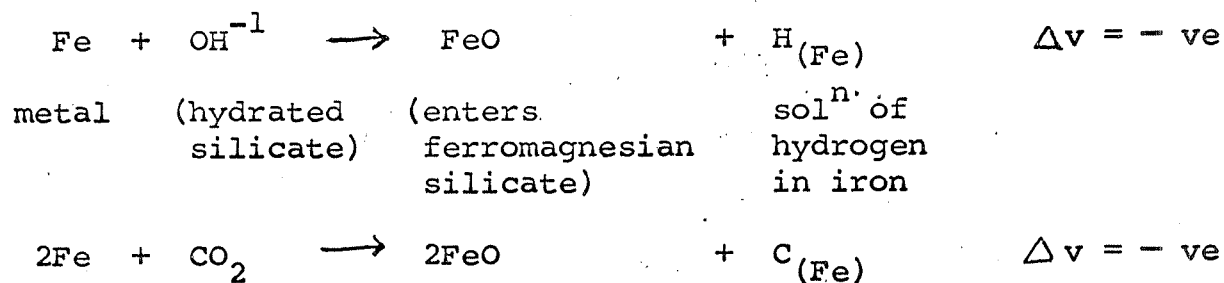potential energy (GPE) (Ringwood 1960, 1966a,b). (The most favourable stage to trap volatiles inside the earth is during the earliest cool period of accretion when the GPE is small). Even if CO_2 and water (as hydrated silicates and carbonates) were present in the material from which the earth accreted, this conventional model would have most of these components degassed at high temperatures (transient or otherwise) during accretion, and in the presence of excess metallic iron. Under these conditions the metallic iron would reduce nearly all the CO_2 and H_2O which is evolved to CO and H_2 with the production of FeO which would enter the silicate fraction.

Suppose that some of the H_2O and CO_2 escaped reduction during impact of the planetesimals and was degassed to form a primitive H_2O - CO_2 atmosphere. Metallic iron particles mixed with silicates of mantle composition [e.g. $(Mg_{.9}Fe_{.1})SiO_4$] falling into this atmosphere with high energies would reduce most of it to CO and H_2. For an average atmosphere temperature of 1000° C the equilibrium ratios of H_2/H_2O and CO/CO_2 would be about 20 (Mueller, 1969).

What would have been the fate of the relatively small amount of CO_2 and H_2O which might have been trapped within the earth during the low-temperature early stage of accretion of the earth when the GPE was relatively small? According to the conventional model, the intimate mixture of silicate and metal particles

accompanied by a small amount of a component containing volatiles is slowly warmed by radioactive heating until partial melting occurs and the metal is able to segregate to form a core.

Before this occurs, we have reduction reactions of the following type (simplified) occurring

$$Fe + OH^{-1} \longrightarrow FeO + H_{(Fe)} \qquad \Delta v = - ve$$

metal   (hydrated   (enters sol^n of
          silicate)   ferromagnesian   hydrogen
                    silicate)   in iron

$$2Fe + CO_2 \longrightarrow 2FeO + C_{(Fe)} \qquad \Delta v = - ve$$

Reduction of CO_2 and H_2O leads to formation of free carbon and hydrogen. However these are soluble (interstitial solutions) in the large excess of metallic iron which is present in the system. Furthermore there are large negative volume changes associated with these reactions so that they are strongly favoured by the high pressures in the earth's interior. The result is that any trapped CO_2 and H_2O is reduced and the resultant carbon and hydrogen are ultimately carried down by the metallic iron into the earth's core. This discussion illustrates only a few of the problems which arise if it is attempted to explain the origin of the earth's hydrosphere and excess volatiles on the basis of those models of accretion of the earth which currently are most widely accepted.

6) Conclusion

Ringwood (1966a,b) concluded that the abundances of Ni, Co, Cu, Au, Pt in the upper mantle, the oxidation state of this region and the nature of the volatiles inferred to be degassed from the upper mantle were not readily explained if the earth had accreted from a well-mixed reservoir of metal and silicate particles in the solar nebula, followed after accretion by segregation of metal into the core. This conclusion still stands.

It is tempting to seek an explanation of these geochemical characteristics in terms of a single unifying hypothesis. All the observations are readily explicable in terms of a simple mixing model. Ringwood (1960, 1966a,b) proposed that the earth accreted sequentially and inhomogeneously from two principal components: (A) a primitive low-temperature component rich in volatiles (including H_2O, CO_2) and oxidized iron, containing siderophile elements in their primordial proportions and (B) a high-temperature component of intensely reduced metal and silicates which was also strongly depleted in volatiles. The earth accreted in a non-equilibrium state and owing to rapid segregation of the core, gross metal-silicate equilibrium, although approached, was not finally reached. Turekian and Clark (1969) have also used a mixing hypothesis based on components A and B, but in a different configuration, to explain the chemistry of the mantle.

Larimer and Anders (1967) have employed a corresponding mixing hypothesis in their interpretation of the chemistry of

chondritic meteorites, and have applied it to the earth. In the latter case, their hypothesis requires that components A and B were well mixed in the solar nebula before accretion of the earth. I have shown above that if the metallic iron component of B greatly exceeds the volatile-rich component A in amount, then their version of the mixing hypothesis fails to explain those aspects of the chemistry of the mantle which have been discussed in this note.

7) Acknowledgements

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